COPROCESSING OF WASTE PLASTICS WITH COAL AND PETROLEUM RESID

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Introduction

Waste plastics have become an increasing problem in the United States since land filling is no longer considered a feasible disposal method. Since plastics are petroleum-derived materials, coprocessing them with coal to produce transportation fuels is a feasible alternative. In this study, catalytic coprocessing reactions were performed using Blind Canyon bituminous coal, Manji and Maya petroleum resids, and plastics. Model polymers including polystyrene, low density polyethylene and poly (ethylene terephthalate) were selected because they represent a substantial portion of the waste plastics generated in the United States. The objective of this research is to determine the effect of using resid as a solvent in the coprocessing of coal and waste polymers on the conversion and product distribution obtained. This study was conducted by first evaluating the reactivity and conversion of the individual systems at coprocessing reaction conditions. Then systems containing binary combinations of either coal, resid, or waste plastic were performed. The last set of reactions performed were ternary systems of coal, resid and waste plastic. All reactions that contained combinations of reactants were reacted catalytically using presulfided $NiMo/Al_2O_3$. The effect of each component on the coprocessing reaction was evaluated.

Experimental

Materials. The model plastic compounds, low density polyethylene (LDPE), polystyrene (PS), and poly(ethylene terephthalate) (PET), used in this study were obtained from Aldrich Chemical Co. and were used as received. The coal used was Blind Canyon bituminous coal (DECS-17) obtained from the Penn State Coal Sample Bank. The proximate analysis of the coal is 45% fixed carbon, 45% volatile matter, 6.3% ash and 3.7% moisture. The ultimate analysis of the coal is 82.1% C, 6.2% H, 0.4% S, 1.4% N, and 0.12%Cl. The resids used were Manji and Maya obtained from Amoco. The analyses of the resids were 85.1% C, 10.8% H, 0.7% N, 2.6% S, 231 ppm V, 220 ppm Ni and 23 ppm Fe for Manji and 84.1% C, 9.9% H, 0.7% N, 5.1% S, 550 ppm V, 100 ppm Ni and 17 ppm Fe for Maya. The solvents used for extraction analyses were HPLC grade hexane, toluene, and tetrahydrofuran (THF) from Fisher Scientific.

Reactions and Procedures. Reactions were performed using a single component, two components, and three components to evaluate the reactivity and mutual effects among the reactants. All reactions were performed in 20 cm^3 stainless steel tubular microreactors at 430 °C for 60 min with 8.3 MPa of H$_2$ introduced at ambient temperature. The microreactors were agitated horizontally at 450 rpm in a fluidized sand bath and were immediately quenched in water after reaction. The reactants were charged at 1.0 g for coal and polymer and 1.5 g for resid, giving resid to polymer and resid to coal ratios of 3:2 in binary system and coal to resid to polymer ratios of 2:3:2 in ternary systems. The coal was stored in a vacuum desiccator before being used. Reactions were performed thermally and catalytically using 1 wt % of powdered, presulfided $NiMo/Al_2O_3$ on a total charge basis. Reactions with LDPE and coal or resid were performed at higher catalysts loadings of 3 and 10 wt %. The $NiMo/Al_2O_3$ catalyst was composed of 2.72 wt % Ni and 13.16 wt % Mo. The procedure for presulfiding $NiMo/Al_2O_3$ began with predrying $NiMo/Al_2O_3$ with N$_2$ for one hr at 300 °C. Then, 10 vol % H$_2$S/H$_2$ gas mixture was flowed over the catalyst at 225 °C for one hr, at 315 °C for one hr, and 370 °C for two hr. The final step was flowing N$_2$ at 370 °C over $NiMo/Al_2O_3$ for one hr.

The reaction products were determined by using solvent fractionation and by weighing the gaseous products. The liquid products were fractionated using a series of solvents into hexane soluble materials (HX); toluene soluble, hexane insoluble material (TOL); and THF soluble, toluene insoluble material (THF), and THF insoluble material or IOM which is defined as insoluble organic matter that is ash-free. Solvent fractionation was also performed on the unreacted materials to determine their solubility. Low recoveries for PS and PET resulted from volatile material being produced during reaction and being lost during the rotary evaporation of hexane. When rotary evaporation was performed at 25 °C with minimal vacuum, the PS reactions products were so volatile that 75% loss occurred while PET lost 67%. The definition for conversion used in this study is the conversion of the reactant to THF soluble material. For coal, the definition for conversion is

$$\% \text{ conversion} = \left[1 - \frac{g\ IOM}{g\ maf\ coal} \right] \times 100 .$$

Plastics and resids have the same definition; however, the plastics are solids at room temperature and have varying but limited solubility in THF, while resids are a semi-solid at room temperature and are totally soluble in THF .

Results and Discussion

The product distributions for the unreacted plastics were determined at ambient temperature to establish a baseline for comparison with their reactivity at coprocessing conditions (Table 1). Previous research performed by Luo and Curtis (1995) has shown that under typical thermal coprocessing conditions only limited conversion of the waste plastics occur. Therefore, the plastics used in this study were reacted under catalytic conditions only using presulfided NiMo/Al$_2$O$_3$. This catalyst was chosen because it has been used almost as a standard in coal liquefaction reactions and because it was used as the catalyst in the waste plastics and waste tire coprocessing pilot scale run performed by HRI and sponsored by the Department of Energy (Pradhan et al., 1994).

Table 1. Product Distributions from Unreacted and Thermally Reacted Material

Reactants[a]	Product Distribution (%)					Conversion (%)	Recovery (%)
	Gas[b]	HX	TOL	THF	IOM		
Unreacted							
PS	0.0	0.0	21.0	14.1	64.9	35.1	112
LDPE	0.0	0.0	1.4	3.1	95.5	4.5	104
PET	0.0	0.0	0.7	0.7	98.6	1.4	104
Manji	0.0	87.1±0.4	12.9±0.4	0.0	0.0	100	103
Maya	0.0	63.0±0.8	37.0±0.8	0.0	0.0	100	101
Thermal Reactions							
Coal	19.1±0.6	15.9±1.1	3.5±0.5	6.2±4.2	55.5±5.4	44.6±5.4	98
Manji	11.6±1.1	71.0±2.1	9.9±0.6	4.9±1.5	2.7±0.1	97.4±0.2	85
Coal/Manji	9.8±0.2	56.9±0.8	8.6±0.4	11.8±1.8	13.1±3.3	87.0±3.3	84

[a] Coal = Blind Canyon DECS-17, Manji and Maya resid. PS = Polystyrene; LDPE = low density polyethylene; PET = poly(ethylene terephthalate). [b] Gas = gaseous product; HX = hexane solubles; TOL = toluene solubles; THF = THF solubles; IOM = insoluble organic matter.

Single Component Reactions. The conversions and product distributions for all of the coprocessing reactions are given in Table 2. The conversions for the single component reactions showed that coal and LDPE yielded lower conversions than the others; their respective conversions were 64.7 and 69.8%. The other plastics, PET and PS, and both resids yielded high conversions, ranging from a low of 94.7% for PET to 100% for PS. A positive influence of the catalyst in the system since coal conversion increased from 44.6% in the thermal reaction to 64.7% in the catalytic reaction. Likewise, when the catalytic conversion of the three plastics are compared to the conversions of the unreacted materials and to the thermal conversions at 440 °C given by Luo and Curtis (1995) the effects of temperature, compared to the unreacted materials, and of catalyst, compared to the thermally reacted and unreacted materials, were positive.

The product distributions of the three plastics reacted at 430 °C with presulfided NiMo/Al$_2$O$_3$ were quite different. Although PS and PET both yielded high conversions, the gas produced from PET was substantially higher yielding 36.8% compared to 8.0% for PS. The yield of hexane solubles from PS was the highest obtained at 91%; however, these hexane soluble materials were very volatile as shown by the low recovery that was discussed in the experimental section. The products produced from the conversion of the plastics were primarily the lighter fractions of gas or hexane solubles. Very small amounts of THF and toluene soluble materials were produced.

The catalytic reaction of the resids produced a small amount of heavier material, IOM and THF soluble material, that was not present in the original resid. The majority of the products were hexane soluble, although the amounts produced were slightly less than in the original resids. At 430 °C and with NiMo/Al$_2$O$_3$, 10 to 15% gas was produced from the resids so that the total amount of hexane solubles and gas produced was equal to the unreacted Manji hexane solubles and higher than the Maya unreacted hexane solubles indicating that Maya was upgraded at these reaction conditions.

Binary Systems. Reactions containing different combinations of the coal, resid, and plastics used in this study were performed, and the conversion and product distributions were obtained. High conversions of 90 to 100% were obtained for the binary combinations of coal plus resid and resid plus polymer, although conversion of resids with LDPE at 77.4 to 80.9% were lower than resid with the

other two plastics. The binary combination of coal and plastics yielded much lower conversions of 47.7 to 66.9% than the other systems, indicating that plastics and coal did not provide a mutually beneficial solvating medium.

Table 2. Reacton Results from Coprocessing Polymers with Coal and Resid[a]

Reactants	Product Distribution (%)					Conversion (%)	Recovery (%)
	Gas	HX	TOL	THF	IOM		
Single Component							
PS	8.0±2.5	91.0±2.7	0.5±0.6	0.5±0.7	0.0	100	42
LDPE	20.0±1.3	41.8±2.8	4.4±1.8	3.6±0.3	30.3±0.6	69.8±0.6	91
PET	36.8±1.6	54.7±1.6	2.0±1.2	1.3±0.1	5.4±1.2	94.7±1.2	56
Coal	18.3±0.1	22.6±1.8	4.2±0.1	19.6±2.5	35.4±3.9	64.7±3.9	94
Manji	10.4±0.4	78.3±0.3	8.5±0.2	1.9±0.6	0.7±0.8	99.3±0.8	85
Maya	14.5±0.4	65.8±0.9	15.1±1.4	1.5±0.4	3.3±0.4	96.8±0.4	93
Two Components							
Coal/Manji	10.8±0.3	64.1±1.6	12.2±0.0	9.7±0.8	3.2±0.6	96.8±0.6	88
Coal/Maya	10.6±0.4	59.4±0.1	20.4±0.1	1.9±0.2	8.0±0.8	92.1±0.8	85
Maya/PS	8.3±0.3	80.4±1.8	8.3±0.6	1.5±0.2	1.7±0.6	98.4±0.6	57
Maya/LDPE	9.5±0.2	58.0±2.0	7.5±0.8	2.5±0.8	22.7±2.2	77.4±2.2	90
Maya/PET	19.0±0.8	65.8±0.1	7.6±0.4	2.4±0.1	5.4±0.4	94.7±0.4	67
Manji/PS	4.7±0.1	86.5±0.9	5.9±0.4	1.4±0.1	1.6±0.6	98.4±0.6	58
Manji/LDPE	9.0±0.3	63.5±0.9	5.7±0.8	2.8±0.1	19.1±0.0	80.9±0.0	89
Manji/PET	18.2±0.4	70.7±0.1	5.5±0.1	1.9±0.1	3.7±0.6	96.3±0.6	63
Coal/PS	7.6±0.1	54.0±2.9	0.8±0.4	2.0±0.5	35.7±2.2	64.4±2.2	56
Coal/LDPE	11.6±1.0	30.1±2.8	4.6±0.1	1.6±0.1	52.3±1.8	47.7±1.8	95
Coal/PET	21.6±0.6	41.6±3.2	1.4±0.6	2.5±1.2	33.1±5.5	66.9±5.5	67
Three Components							
Coal/Maya/PS	7.7±0.4	69.2±0.8	9.4±0.5	5.9±0.1	8.0±0.9	92.1±0.9	66
Coal/Maya/LDPE	9.0±1.8	52.9±2.1	9.1±0.0	5.7±0.1	23.4±0.4	76.7±0.4	90
Coal/Maya/PET	16.9±1.5	55.9±2.5	7.5±0.0	6.8±0.1	13.0±0.9	87.1±0.9	74
Coal/Manji/PS	5.4±0.4	75.5±1.7	7.5±0.4	6.6±0.2	5.2±1.6	94.8±1.6	62
Coal/Manji/LDPE	9.4±1.9	57.2±1.1	9.1±0.6	5.0±0.0	19.4±0.3	80.6±0.3	88
Coal/Manji/PET	14.9±0.1	61.6±0.6	7.1±0.4	7.0±0.0	10.1±1.1	89.9±1.1	71
Two Components at Higher Catalyst Loading							
Coal/LDPE	10.7±0.4	36.1±1.8	3.5±0.2	3.8±1.3	46.0±2.6	54.1±2.6	90
Maya/LDPE	9.2±0.1	57.4±0.5	6.9±0.9	3.2±0.6	23.5±0.4	76.6±0.4	90
Manji/LDPE	8.3±0.1	61.0±1.5	4.1±0.1	2.2±1.3	24.5±0.1	75.5±0.1	93
Three Components at Higher Catalyst Loading							
Coal/Manji/LDPE	6.9±0.1	60.7±1.1	8.4±0.3	4.7±0.6	19.4±0.6	80.7±0.6	88

[a] Reaction Conditions 430 °C, 8.3 MPa H_2, and one hour; 1 wt% NiMo/Al$_2$O$_3$ of total feedstock for catalytic reactions.

A parameter, termed coprocessing effect factor (f_i), was defined that evaluated the effect of combining two materials rather than reacting them individually. The three coprocessing effect factors that were evaluated were the conversion, hexane soluble, and gas coprocessing effect. The equation that defines this parameter is

$$f_i = \frac{(\% \, CP_i - \% \, HM_i)}{\% \, CP_i} \times 100$$

where i is either gas, hexane solubles, or conversion, HM is the hypothetical mean, and CP is the coprocessing result.

The reactions of coal and resid showed positive coprocessing effect factors for hexane solubles and conversion which means that more hexane soluble material was produced and more conversion of material occurred when coal and resid were reacted together than when they were reacted individually. The coprocessing effect factor for gas products was negative for both coal and resid combinations, meaning that less gas was produced during coprocessing than in the individual reactions. Similarly, the reaction of Maya resid with each of the plastics resulted in each binary

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combination having a positive hexane soluble coprocessing effect factor and negative gas coprocessing effect factor. The conversion coprocessing effect factor for Maya and the three plastics varied according to the type of plastic: Maya and PS gave a slightly positive factor while the other two combinations gave negative values. Manji resid reacted with each of the three plastics resulted in a less positive hexane coprocessing effect factor than Maya/polymer and large negative values for the gas coprocessing effect factor. The combination of coal and PS or LDPE was detrimental to the production of hexane soluble material from the coprocessed materials, while the combination of coal with PET was favorable for the production of hexane soluble material. The amount of gas produced during coprocessing was less with the coal and polymers as it was with combined reaction of all the other systems. The coprocessing effect factor for conversion of the coal and polymer systems yielded negative values that were quite large ranging from −19.1 for coal and PET to −41.0 for coal and LDPE. The combination of coal and polymer was detrimental to the conversion compared to that obtained in individual reactions.

Ternary Systems. The coprocessing effect factors for the ternary systems were calculated two ways. The first method of calculation shown on Table 3 used the hypothetical mean of the individual reactions where the ratio of the components in the ternary system was used to weight the various terms. The second method of calculating the hypothetical mean was to use the results of reactions of a single component and a binary system to calculate hypothetical mean in which of the reactants involved were weighted according to the relative amount of each material in the ternary systems.

The results with the calculational method using the individual reactions are given in Table 3. All of the ternary reaction systems showed a positive coprocessing effect factor for the hexane soluble material when compared to the hypothetical mean calculated from the individual reaction systems. The gas coprocessing effect factor for each ternary reaction system resulted in large negative values. Particularly, the ternary systems containing PS and LDPE gave large negative values; PET also gave negative values but the decrease compared to the individual systems was not nearly as large. Reacting the three components yielded a much reduced gas make compared to the individual reactions. Coprocessing the three materials together resulted in positive effects on the conversion of ternary systems containing PS and PET for both coal and resid combinations; however, the systems containing LDPE gave negative values. Reaction with Manji resid was more beneficial to each of the polymers than was Maya.

The coprocessing effect factor calculation with the hypothetical mean from the single component plus binary systems gave negative gas coprocessing effect factors. The hexane soluble coprocessing effect was positive for the coal plus resid/polymer systems and for the resid plus coal/polymer systems; however, only half the polymer plus coal/resid systems gave positive values. LDPE gave negative values for both resids indicating that the binary system did not increase the hexane solubles compared to the hypothetical mean. The conversion coprocessing effect factor was positive for the hypothetical means using coal plus resid/polymer and resid plus coal/polymer. However, all of the conversion coprocessing effect factors for polymer plus coal/resid were negative, indicating that addition of the polymer to the coal/resid system was detrimental to overall conversion.

Effect for Catalyst Loading. The binary and ternary systems containing LDPE gave lower conversions and hexane solubles than the other polymers. The effect of increasing catalyst loading to 3 and 10 wt % based on the total charge on coal conversion and hexane soluble yield in binary and ternary systems containing LDPE was determined. The 3 wt % addition increased the conversion in the coal/LDPE from 47 to 54 % (Table 2); the effect on conversion from the other binary and ternary systems were minimal and with the resids even decreased the conversion slightly. Increasing the catalyst loading to 10 wt % had a similar effect as the 3% loading.

Summary and Conclusions

The coprocessing of coal, plastics and resid yielded favorable results. The amount of gas produced decreased as the number of components in the reaction increased. For binary and ternary systems containing resid, increases in the amount of hexane solubles and in conversion were apparent. The binary reaction of coal and plastics did not show this effect; the combination appeared to be detrimental to both materials. However, when resid was added to the system in the ternary systems, the positive hexane soluble and conversion coprocessing effect factors were obtained. Increasing catalyst loading improved the conversion of and the hexane soluble yield in the coal/LDPE system. Increased catalyst loading had little effect on the binary and ternary systems containing resids.

Table 3. Coprocessing Effect Factors for Binary and Ternary Systems

Reaction Combinations	Coprocessing Effect Factor (f)		
	Gas	HX	Conversion
Two Components			
Coal/Manji	-25.6	12.6	11.7
Coal/Maya	-51.1	18.3	8.8
Maya/PS	-43.4	5.6	0.3
Maya/LDPE	-75.8	3.1	-11.1
Maya/PET	-15.2	6.8	-1.3
Manji/PS	-100.9	3.6	-1.2
Manji/LDPE	-58.2	-0.3	-8.2
Manji/PET	-15.2	2.6	-1.2
Coal/PS	-73.0	-5.2	-27.9
Coal/LDPE	-65.1	-7.0	-41.0
Coal/PET	-27.5	7.1	-19.1
Ternary Systems with Hypothetical Mean of Individual Components[b]			
Coal/Maya/PS	-78.3	12.4	3.9
Coal/Maya/LDPE	-90.6	11.9	-4.2
Coal/Maya/PET	-29.9	10.1	0.1
Coal/Manji/PS	-121.7	12.6	5.5
Coal/Manji/LDPE	-63.8	9.2	-0.5
Coal/Manji/PET	-35.6	9.7	2.0
Ternary Systems with Hypothetical Mean of Single and Binary Systems[b]			
Coal + Maya/PS	-44.9	7.7	3.6
Coal + Maya/LDPE	-33.5	9.5	3.8
Coal + Maya/PET	-11.2	4.4	1.1
Coal + Manji/PS	-59.0	9.6	6.4
Coal + Manji/LDPE	-24.0	9.4	5.4
Coal + Manji/PET	-22.3	7.5	2.9
Maya + Coal/PS	-37.1	14.7	15.0
Maya + Coal/LDPE	-42.7	14.2	10.4
Maya + Coal/PET	-9.8	7.0	8.5
Manji + Coal/PS	-63.0	14.7	16.3
Manji + Coal/LDPE	-18.0	11.3	13.4
Manji + Coal/PET	-12.8	6.9	10.1
PS + Coal/Maya	-28.0	1.1	-2.5
PS + Coal/Manji	-85.2	4.9	-3.1
LDPE + Coal/Maya	-47.6	-2.8	-11.8
LDPE + Coal/Manji	-42.9	-0.9	-10.5
PET + Coal/Maya	-7.0	-3.9	-6.6
PET + Coal/Manji	-22.3	0.3	-7.0

[a] HM = Hypothetical Mean of reactants which is defined as

$$HM_i = \frac{(\% \ coal_i + 1.5 \ x \ \% \ resid_i + \% \ polymer_i)}{total \ charged \ (g)}$$

[b] Calculations using different hypothetical mean which is defined as

$$HM_i = \frac{(x) \times \% \ one \ component + (y) \times \% \ two \ components}{3.5}$$

where x is 1.0 for coal and polymer and is 1.5 for resid; y is 2.0 for coal and polymer and 2.5 for resid.

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